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Communications to the Editor

Dimerization of Silaethylene: Computational Evidence for a Novel Mechanism for the Formation of 1,3-Disilacyclobutane via a 1,2 Approach

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It is now established, both computationally[1] and experimentally,[2,3] that forbidden $[2\pi + 2\pi]$ cycloadditions proceed via a stepwise mechanism involving the formation of a short-lived 1,4 biradical intermediate. The rapidity of the recoupling of the two radical centers in the trans tetramethylene biradical intermediate to generate the cyclobutane product by rotation about the central σ bond has recently been confirmed in an elegant experiment by Zewail et al., who demonstrated that the lifetime of this species cannot exceed a few hundred femtoseconds.[4] In this paper, we report a completely different mechanism for the stepwise dimerization of silaethylene which involves a low-barrier [1,2] silyl sigmatropic shift which is competitive with the normal fast rotation−recoupling ring closure seen in the tetramethylene biradical.

Current mechanistic theory suggests that only stable silaethylenes (i.e., more heavily substituted silaethylenes in which the π bond polarization is lost) dimerize via a stepwise biradical mechanism to produce 1,2-disilacyclobutane (1,2-DSCB), while unstable silaethylenes (i.e., the parent silaethylene and those carrying small alkyl substituents in which the π bond is heavily polarized to the carbon) dimerize via a concerted $[2\pi_s + 2\pi_s]$ mechanism to form 1,3-disilacyclobutanes (1,3-DSCB).[5] Recently, however, a mechanism for head-to-head and head-to-tail dimerization of silaethylenes (in which, the π bond is polarized) to produce 1,2-disilacyclobutane (1,2-DSCB) and 1,3-disilacyclobutane (1,3-DSCB) involving the formation of $CH_2{-}SiH_2{-}SiH_2{-}CH_2$ and $CH_2{-}SiH_2{-}CH_2{-}SiH_2$ biradicals[1b−6] has been documented.

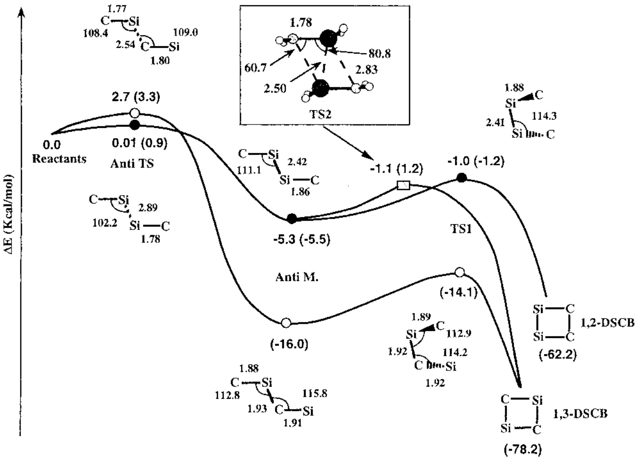

Figure 1. Energy profiles and relevant geometrical parameters (bond lengths in Å and angles in deg) of the three reaction paths. Black and white circles indicate stationary points on the head-to-tail and the head-to-head path, respectively. The gray box indicates the rhomboid transition state on the [1,2] silyl sigmatropic shift path. The relative energies (kcal mol^{-1}) correspond to the CASPT2/6-311G* + ZPE values, while bracketed values correspond to CASPT2/6-31G* + ZPE values.

The energy profiles of the chemically relevant reaction paths together with few important geometrical parameters are shown in Figure 1[9] for the stepwise biradical pathways (head-to-head and head-to-tail) for the dimerization of the parent silaethylene corresponding to the prototype polarized silene. These profiles were obtained from full CASSCF optimizations[7] at the 6-31G* level using an active space of eight electrons and eight orbitals (the π and π^* orbitals of the π systems and the σ and σ^* orbitals associated with the C−Si bonds) where the energy has been corrected by multireference perturbation theory (CASPT2[8]). A few mechanistically important points were recomputed at the 6-311G** basis set level (CASPT2/6-311G**//CASSCF/6-31G*). The results reveal that the head-to-head biradical not only reacts via a rotation−recoupling mechanism but also rearranges via a [1,2] silyl sigmatropic shift leading to 1,3-disilacyclobutane (1,3-DSCB). All the geometrical parameters for the various critical points including the two products 1,3-DSCB and 1,2-DSCB are given in the Supporting Information.

The results obtained for the head-to-head and head-to-tail paths are very similar to those previously reported.[5] Both an anti and a gauche transition state have been located together with the two corresponding biradical intermediates (*anti*-**M** and *gauche*-**M**[9]). These intermediates are interconnected by a conformational transition state (*anti/gauche*-**TS**[9]) and can evolve to the product through another transition state, denoted as **TS1**. In addition to

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[8] *MOLCAS* Version 3.0: K. Andersson et al., University of Lund, Sweden, 1994.

[9] The relative energy values in Figure 1 were computed at the CASPT2/6-311g**+ZPE (CASSCF/6-31g*) level. Full details on the CASSCF, CASPT2F, and ZPE energies are shown in Table I of the Supporting Information.

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these two biradical mechanisms, we have characterized an additional completely novel pathway which involves a rhomboid transition state for a [1,2] silyl sigmatropic shift, where the migration of one Si−Si σ bond brings about the simultaneous formation of two σ Si−C bonds. This transition state, denoted as **TS2,** connects the head-to-head *anti*-**M** to the 1,3-DSCB product. The corresponding reaction path (see Figure 1)has been characterized by an intrinsic reaction coordinate calculation.

A rhomboid transition structure for this reaction was previously computed by Seidl et al. at the CCSD level of theory.[5c] Given the similarity of such a structure with our **TS2**, it seems now to be established that both the CASSCF and CCSD calculations locate the same transition structure. This conclusion is in contrast with our previous suggestion that this structure is an artifact of the CCSD computational level.[6] The confusion arises from the transition vectors. In fact, Seidl et al. have associated their structure to a transition vector computed at the SCF level which describes a concerted dimerization process while our CASSCF calculations indicate that the correct process is a [1,2] sigmatropic shift (see footnote 10 for further details). Similar transition states have also been reported for the dimerization of ethylene[11] and the thermal decomposition of silacyclobutane.[12]

Regardless the unfavorable energy, which makes such transition states mechanistically irrelevant, these findings show that rhomboid structures can be detected in other $[2\pi + 2\pi]$ cycloadditions. On the other hand, when silenes are involved in the dimerization, these rhomboid structures become increasingly favorable. In fact, while a [1,2] sigmatropic shift mechanism does not play a role in alkene $[2\pi + 2\pi]$ cycloadditions, its existence in silaethylene is not completely unexpected. The simultaneous formation of two Si−C bonds as an alternative to the breaking of the single weaker Si−Si bond carries a certain energetic advantage. Moreover, the 1,2 migration, from Si to C in free radicals, has already been experimentally observed.[13]

The energetics[9] given in Figure 1 indicate that the activation energies are very small in all cases. The head-to-head approach, being virtually barrierless (0.01 kcal mol^{-1}), is favored with respect to the head-to-tail approach, which is characterized by an activation barrier of 2.7 kcal mol^{-1}. The lowest energy path that leads to the formation of 1,3-DSCB follows the head-to-head path up to the formation of the *anti*-**M** and then bifurcates following a silyl sigmatropic 1,2 shift path that goes through the rhomboid TS (**TS2**). At the best level of theory, the **TS2** becomes slightly lower in energy than the rotation−recoupling transition structure **TS1**, and both transition states lie below the head-to-head anti fragmentation barrier. These results suggest that both cyclic products can be formed simultaneously and that the [1,2] silyl sigmatropic shift is a pathway competitive with the normal ring closure to 1,2-DSCB.

These data are compatible with the experimental results. The experimental study by Maier, Mihm, and Reisenauer[14] reveals that silaethylene certainly dimerizes to 1,3-DSCB but does not exclude the competitive formation of 1,2-DSCB. Similar indications have been obtained in the low-pressure dimerization of a simple silaethylene such as $Me_2Si{=}C(Me)(SiMe_3)$ where products arising from both the head-to-head and the head-to-tail dimerization were also observed.[15] The 1,3-DSCB product is more stable than the 1,2-DSCB product by 16 kcal mol^{-1}.

In summary, a completely novel mechanism for the stepwise dimerization of the parent silaethylene has been detected. This mechanism involves a low-barrier [1,2] silyl sigmatropic shift that becomes competitive with the rotation−recoupling closure mechanism, the fast processes which bring the tetramethylene radicals to the cyclic products. The involvement of a [1,2] silyl sigmatropic shift in the dimerization mechanism leads to a better interpretation of experimental data regarding the competition between head-to-tail and head-to-head paths in the dimerization of silenes. The formation of both products can be competitive. Both mechanisms follow the head-to-head approach in the first part of the reaction, then the 1,2 product is formed via the normal rotation−recoupling path, while the 1,3 product is formed mainly via the 1,2 shift path involving the rhomboid transition state **TS2.**

Supporting Information Available: Full details on the CASSCF, CASPT2F, and ZPE energies (7 pages). See any current masthead page for ordering and Web access instructions.

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(10) This difference is due to the fact that Seidl et al. have optimized the transition state geometry at both SCF and CCSD levels but they have computed the transition vector at the SCF level only. In contrast, we have now computed both the geometry and transition vector at the same level of theory (CASSCF). We were also misled by the fact that their SCF-optimized TS structure is very similar to a rhomboid conical intersection (see ref 6).

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